The Derjaguin Approximation.

(How to account for curvature)

- Consider 2 spheres of radii \( R_1 \) & \( R_2 \) separated by \( h \). \([h \ll R_1, R_2]\)

Distance between rings \((Z) = z_1 + h + z_2\)

Now: \( F(h) = \int \frac{dA}{2\pi h} \left( \frac{F}{A} \right) dx \)

\( Z = h \)

Limit in \( Z \)

(Recall \( \frac{F}{A} \) is a function of separation distance \( h \))
How to get from $x$ to $z$.

- **Chord theorem**:

\[ x^2 \theta = (2R-z)z \approx 2Rz \quad (z \ll R) \]
\[ x^2 \theta^2 = 2R \theta_1 \theta_2 = 2R_2 z \quad (constant \ \theta \ \text{for integration}) \]

Now, \[ z_1 = \frac{x^2}{2R_1} \quad z_2 = \frac{x^2}{2R_2} \]

\[ Z = z_1 + h + z_2 = \frac{x^2}{2R_1} + h + \frac{x^2}{2R_2} \]

\[ Z = h + \frac{x^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]

\[ dZ = \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \kappa \ dx \]

\[ \kappa \ dx = \frac{dZ}{\left( \frac{1}{R_1} + \frac{1}{R_2} \right)} = \left( \frac{R_1 R_2}{R_1 + R_2} \right) dZ \]
Back to integral:
\[
F(h) = \int_{Z=h}^{Z=\infty} 2\pi x \left( \frac{E}{A} \right) dx = \int_{h}^{\infty} 2\pi \left( \frac{E}{A} \right) \left( \frac{R_1 R_2}{R_1 + R_2} \right) dZ
\]

\[
F(h) = 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) \int_{h}^{\infty} \left( \frac{E}{A} \right) dZ
\]

OK, now define the energy of interaction:
\[
U(h) = \int_{\infty}^{h} F(x) dx
\]

\[
F = -\frac{dU}{dx}
\]

\[
F(h) = 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) \frac{U(h)}{A}
\]

\[
F < dh = 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) U \quad \text{flat plates}
\]

"Derjaguin approx."
- Very important relationship ... handles changes in geometry.
- Valid for any type of force profile, as long as \( h \ll R \). (Where would it not work?)
- Often, easiest to derive energy of int. for flat plates & force between spheres more practical.

\[ \frac{E}{A} (h) = 64kT \cos^4 \tanh^2 \left( \frac{2e\phi_0}{4kT} \right) \exp(-\Phi h) \]

\[ \frac{E}{A} (h) = B \exp(-\Phi h) \quad \equiv \text{"B"} \]

\[ \frac{U_{\infty}}{A} = \int_{h}^{\infty} \frac{E}{A} (h) \, dh' = \int_{h}^{\infty} B \exp(-\Phi h') \, dh' \]

\[ \frac{U_{\infty}}{A} = -\frac{B}{\Phi} \left[ \frac{1}{\exp(\Phi h)} \right]_h^{\infty} = \frac{B}{\Phi} \left[ \frac{1}{\exp(\Phi h)} \right]_h^{\infty} \]

\[ \frac{U_{\infty}}{A} = \frac{B}{\Phi} \exp(-\Phi h) \]
- Now, Derjaguin:

\[ F_{ss}(h) = 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) \frac{U_{ww}(h)}{\text{area}} \]

\[ F_{ss}(h) = 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) \left( \frac{B}{\mu} \right) \exp \left(-\frac{h}{\kappa} \right) \]

EDL energy between spheres, weak overlap limit.

- Energy between spheres:

\[ F = -\frac{\partial U}{\partial h} \]

\[ U_{ss}(h) = \int_{h}^{\infty} F_{ss}(h) \, dh' \]

\[ = \int_{h}^{\infty} 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) \left( \frac{B}{\mu} \right) \exp \left(-\frac{h'}{\kappa} \right) \, dh' \]

\[ U_{ss}(h) = 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) \left( \frac{B}{\mu^2} \right) \exp \left(-\frac{h}{\kappa} \right) \]

EDL energy between spheres, weak overlap limit.
- Other forms of Derjaguin:

\[
F_{sw}(h) = 2\pi R \frac{U_{sw}(h)}{A} \quad (R_2 \to 0).
\]

\[
F_{xc}(h) = 2\pi \sqrt{R_1 R_2} \frac{U_{sw}(h)}{A}
\]

(others exist).

- Van der Waals interactions between macroscopic
  
- Interparticle van der Waals interactions.

Recall that:

\[
V_{ij}(r) = -\frac{C_1}{r^6} \quad \text{(VDW int.)}
\]

\(C \propto \alpha_1 \alpha_2 \cdot \cdot \cdot \)

- To calculate the interaction between two particles, we'll first assume we can just add all contributions from VDW. (Pairwise additivity, only really valid for like kinds of particles.)
Now, for two semi-infinite slabs...

\[ dU_{12} = -C_{12} \rho_1 \rho_2 \frac{dV_1 dV_2}{\left( (\eta_2 - \eta_1)^2 + (\nu_2 - \nu_1)^2 + (z_2 - z_1)^2 \right)^{\frac{3}{2}}} \]

\[ U_{12} = C_{12} \rho_1 \rho_2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{dV_1 dV_2}{\left( (\eta_2 - \eta_1)^2 + (\nu_2 - \nu_1)^2 + (z_2 - z_1)^2 \right)^{\frac{3}{2}}} \]

solve by subst. \( \eta = (\eta_2 - \eta_1) \)

\( \eta' = (\eta_2 + \eta_1) \)

\( \nu = (\nu_2 - \nu_1) \)

\( \nu' = (\nu_2 + \nu_1) \)
\[
\frac{U_{ww}(h)}{\text{area}} = \frac{U_{2}}{\text{dndy}} = (4\pi \rho \rho_{2} \pi) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dx\, dy\, dz_{1}\, dz_{2}}{(x^{2}+y^{2}+(z_{2}-z_{1})^{2})^{3}}
\]

\[
\frac{U_{ww}(h)}{\text{area}} = -\frac{(4\pi \rho \rho_{2} \pi)}{12} \left( \frac{1}{h^{2}} \right)
\]

Define a material-dependent "Hamaker constant" ... 

\[H_{12} = \pi^{2} \cdot C \rho \rho_{2} \]

\[
\frac{U_{ww}(h)}{\text{area}} = -\frac{H_{12}}{12\pi} \left( \frac{1}{h^{2}} \right) \quad \text{(VDW energy of incl. between flat plates)}
\]

\[
\frac{U_{sw}(h)}{\text{area}} = -\frac{H_{12}R}{6} \left( \frac{1}{h} \right) \quad \text{(sphere-wall VDW energy)}
\]

\[
U_{ss}(h) = -\frac{H_{12}}{6\pi} \left( \frac{R_{1}R_{2}}{R_{1}+R_{2}} \right) \left( \frac{1}{h} \right) \quad \text{(sphere-sphere VDW energy)}
\]

\[
U_{kc}(h) = -H_{12} \sqrt{R_{1}R_{2}} \left( \frac{1}{f} \right) \quad \text{(crossed-cylinders)}
\]
- So what is this Hamaker constant?

- Units of energy. $H_{12} = 10^{-19} \sim 10^{-20}$ J

$H_{12} \times 10^{20}$ J

<table>
<thead>
<tr>
<th>Material</th>
<th>$H_{12} \times 10^{20}$ J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>4.35</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>7.8  ~ 9.8</td>
</tr>
<tr>
<td>Silver</td>
<td>39.8</td>
</tr>
<tr>
<td>Gold</td>
<td>45.3</td>
</tr>
<tr>
<td>n-octane</td>
<td>4.5</td>
</tr>
<tr>
<td>liquid He</td>
<td>0.057</td>
</tr>
</tbody>
</table>

- What about interactions across a medium?

\[
\begin{array}{c}
\text{Au} \\
\text{H}_2\text{O}
\end{array}
\quad \quad
\begin{array}{c}
\text{Au} \\
\text{H}_2\text{O}
\end{array}
\]

"1" "3" "1"
What is the Hamaker Constant Related to?

London Forces

\[ V_{ij\text{, London}}(R) = -\frac{3}{2} \left( \frac{I_1 I_2}{I_1 + I_2} \right) \left( \frac{\alpha_1 \alpha_2}{(4\pi \varepsilon_0)^2} \right) \frac{1}{R^6} \]

Pairwise Summation (of Keesom + Debye Forces)

Hamaker Constant

Polarizability

Both London Forces & Hamaker Constant function of Material Polarizability

\[ \alpha \leftrightarrow \text{Macroscopic} \]

use Lorentz-Lorenz Eqn.

\[ \frac{\alpha}{(4\pi \varepsilon_0)} = \left( \frac{n^2 - 1}{n^2 + 2} \right) \frac{3 \, V}{4\pi} \]

\( n \) is Index of Refraction
The Hamaker constant is related to the index of refraction!

The magnitude of $H_{12}$ between materials is proportional to the difference in $n_1$ and $n_2$

$$|H_{12}| \propto |n_1 - n_2|$$

In a practical sense:

**Hamaker constant between**

- PS water PS
- Au water Au
- Oil water Oil

$\text{HamakerConst}$

- PS 1.515
- Water 1.33
- Oil ~ 1.4
- Au $\gg 1$

$\Rightarrow$ HamakerConst.

$H_{\text{gold}} > H_{\text{PS}} > H_{\text{Oil}}$
- "Combining relations" (Based on Lifschitz Theory of London Int.)

\[
\begin{align*}
A_{12} & \equiv \sqrt{H_{11} \cdot H_{33}} \\
\Rightarrow & \text{ in vacuum.}
\end{align*}
\]

\[
H_{131} \equiv H_{313} \equiv H_{11} + H_{33} - 2H_{13}
\]

For like materials always attractive (always ultradielectric).

\[
H_{132} \equiv \left[ \sqrt{H_{11}} - \sqrt{H_{33}} \right] \left[ \sqrt{H_{22}} - \sqrt{H_{33}} \right]
\]

(can be positive or negative!)

ex) Quatz/olivine/quartz

\[
\begin{align*}
H_{\text{oil}} & = 4.5 \times 10^{-20} \text{ J} \\
H_{\text{quartz}} & = 6.3 \times 10^{-20} \text{ J}
\end{align*}
\]

\[
H_{131} = H_{11} + H_{33} - 2H_{13} = H_{11} + H_{33} - 2\sqrt{H_{11} \cdot H_{33}}
\]

\[
= 6.3 + 4.5 - 2\sqrt{6.3 \times 4.5} = 0.15 \times 10^{-20} \text{ J}
\]

c) Quartz / octane / air. \( h_{air} = 0 \) (ideal gas law).

\[
H_{132} = (\sqrt{H_{41}} - \sqrt{H_{32}})(\sqrt{H_{22}} - \sqrt{H_{33}}) \\
= (\sqrt{6.3} - \sqrt{4.5})(0 - \sqrt{4.5}) \\
= \boxed{-0.82 \times 10^{-20} J} \quad \text{incl. between quartz} \\
\text{and octane are stronger!}
\]

- Other issues:
  - Retardation: at distances >5 nm, \( \tau \) to deviation.
    \( \alpha = \frac{1}{\tau} \) or greater
    
    (due to the distance to travel from 1 to 2 = time for fluctuations)
  
- Darwin additivity only good for London, but error is lumped in \( H_{12} \).
  
- Difficult to measure experimentally, but not impossible.
  
- Maybe hard to measure, but vital to dispersion stability.